

# PATENT SPECIFICATION

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## (54) ELASTOMERIC BLOCK COPOLYMERS AND METHODS OF PRODUCING SAME

(71) We, INSTITUT NEFTEKHIMICHESKOGO SINTEZA IMENI A. V. TOPCHIEVA AKADEMII NAUK SSSR, a Russian state enterprise organised and existing under the laws of the United Socialist Soviet Republic, of Leninsky prospekt, 29, Moscow, U.S.S.R. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new types of elastomeric block copolymers which can be utilized over a wide range of operating temperatures and methods of producing the same.

A series of elastomeric block copolymers of the structural type A—B—A is known where block A is a non-elastomeric polymer of a monoalkenyl aromatic hydrocarbon and block B an elastomeric polymer of a conjugated diene hydrocarbon (cf. Brit. pat. 1,000,090; 1,014,999; 1,025,295; Fr. pat. 1,459,399).

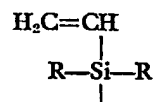
One of the disadvantages of these prior art block copolymers of the A—B—A type is the low glass-transition temperature of block A, as a consequence of which their use at high temperatures (e.g. at temperatures higher than 80°C) is impossible.

It is an object of the present invention to provide new polymeric materials of the A—B—A type which can be used over a wide range of operating temperatures from -80° to +150°C or higher.

According to the invention there is provided a block copolymer of the A—B—A type where block B is a polymer of a conjugated diene, while each block A, according to the invention, is a polymer of a vinyltriorganosilane or a copolymer of a vinyltriorganosilane and styrene or a substituted derivative of styrene. Such a block A has an average molecular weight of from 5,000 to 200,000 and a glass-transition temperature of 95 to 180°C. In the A—B—A block copolymer, the

polymeric blocks A may constitute from 10—50% by weight of the weight of the block copolymer.

For producing block A, vinyltriorganosilanes of the following structure are used:

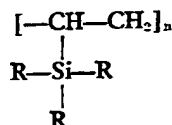


where R represents identical or different organic radicals, e.g. alkyl radicals of normal or branched structure with one to four carbon atoms, aryl or substituted aryl or naphthenic radicals. For producing block A there can be used monomers as vinylthyldimethylsilane, vinylbutyldimethylsilane, vinyltrimethylsilane and vinylphenyldimethylsilane, as well as copolymers of said monomers and styrene or its substituted derivatives.

Further, according to the invention there is provided a method of producing a block copolymer of the A—B—A type comprising copolymerising a conjugated diene with a vinyltriorganosilane or a mixture of a vinyltriorganosilane and styrene or a substituted styrene in the presence of a lithium or organolithium catalyst.

Preferably, the method includes the steps of polymerizing a vinyltriorganosilane or copolymerizing a vinyltriorganosilane and styrene or a substituted styrene to form block polymer A having a molecular weight of from 5,000 to 200,000 adding a conjugate diene and continuing the polymerization to form block B having a molecular weight of 15,000 to 500,000, after which a further addition is made of said vinyltriorganosilane or a mixture of vinyltriorganosilane and styrene or a substituted styrene.

In the above conditions there are produced non-elastomeric high-molecular weight compounds of the following structure:



The process of producing silicon-containing block copolymers of the type A—B—A can be carried out in the presence of the following anionic polymerization catalysts: metallic lithium, lithium alkyls or other organo-lithium compounds. The alkyls in said lithium alkyls are preferably branched, e.g. isopropyllithium, sec. butyllithium, isobutyllithium, isoamyllithium, etc., owing to their high velocity of reaction with vinyltriorganosilanes.

Block copolymerization may be carried out in hydrocarbon solvents: lower alkanes of normal and iso-structure containing from 5 to 10 carbon atoms, aromatic and cycloaromatic hydrocarbons or mixtures of the same, e.g. hexane, cyclohexane, benzene, toluene, or mixtures of the same may be used.

In the presence of metallic lithium or lithium-organic compounds in the above-mentioned hydrocarbon solvents there is obtained a high content of elastomeric block B of 1,4-cis structure which has a molecular weight within the range from 15,000 to 500,000. Polymerization may be carried out at temperatures from 0° to 70°C.

The concentration of the catalyst can vary within a wide range, depending on the required molecular weight of the block copolymer, e.g. from 0.001 mol/l to 0.1 mol/l.

In order to obtain the best elastic properties in the block copolymer, the non-elastic terminal blocks A should have a molecular weight within the range from 10,000 to 80,000, with a glass-transition temperature within the range from 100 to 180°C. Elastomeric block B should suitably have an average molecular weight within the range from 15,000 to 500,000 with a glass-transition temperature from -50 to -90°C.

Polymerization can be carried out in vacuum (from 10<sup>-1</sup> to 10<sup>-5</sup> mm of mercury) or in an atmosphere of a dry and purified inert gas, e.g. nitrogen, argon, etc.

The block copolymer of the general formula A—B—A can be produced in two ways: by the consecutive addition of monomers, or by employing coupling substances.

The consecutive process of adding monomers is carried out as follows.

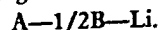
In the first stage there is produced in the presence of a lithium-based catalyst and an organic solvent a non-elastomeric polyvinyltriorganosilane block A, e.g. polyvinyltrimethylsilane polymer having a terminal lithium ion, a so-called living polymer. This stage is completed when the free catalyst and monomer are completely exhausted. In the second stage there is added a conjugated diene,

e.g. butadiene or isoprene which grows on the polymeric chains of block A, forming elastomeric block B. Block B also has a lithium ion at the ends of the polymeric chains, and after completion of diene polymerization a block copolymer of the structure A—B—Li is obtained. In the third stage there is again added vinyltriorganosilane, which grows on the polymeric chains A—B—Li to form the terminal non-elastomeric block A.

In a variation of this process metallic lithium is employed. In this case there is first obtained in an organic solvent an intermediate elastomeric conjugated diene block B with lithium ions at the ends of the chains: Li—B—Li. This stage is completed when the conjugated diene has been completely exhausted. Vinyltriorganosilanes or a mixture of vinyltriorganosilanes and styrene or derivatives of styrene are then added and polymerization continued until the monomer has been completely exhausted, block A growing simultaneously on both ends of block B to give the final product A—B—A. Thus, the process is carried out in two stages.

In block copolymerization employing coupling substances, there is obtained in the first stage of the process, as in the consecutive process, non-elastomeric block A, e.g. polyvinyltrimethylphenylsilane having lithium ions at the ends of the polymeric chains.

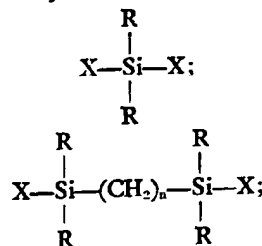
In the second stage there is added to the living chains of block A the required amount of conjugated diolefin, e.g. isoprene, and after completion of the polymerization of said diolefin there is formed a living block copolymer of the general formula



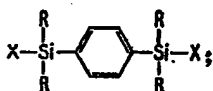
The next stage in this process is joining these intermediate block copolymers to give a substance of twice the molecular weight having the formula A—1/2B—C—1/2B—A, where C is the residue of the coupling agent.

This reaction proceeds satisfactorily when dihaloid derivatives of hydrocarbons having 1 to 10 carbon atoms are employed as coupling agents, e.g. 1,2 - dibromoethane, 1,4 - dibromobutane, 1,10 - dibromodecane, etc.

We have found, and it is a part of the teaching of the present invention, that as highly effective coupling agents there may be employed organosilicon bifunctional compounds suitably of the following structures:



and



where

X is Br, Cl, OR, OH, H;  
n=1-6;

- 5 R is like or unlike alkyl radicals of normal or branched structure having 1 to 16 carbon atoms, or aryl or substituted aryl or naphthenic radicals.

- 10 The higher effectiveness of said coupling agents is due to the fact that the bonds  $\equiv\text{Si}-\text{X}$ ,  $\equiv\text{Si}-\text{H}$ ,  $\equiv\text{Si}-\text{OR}$  and  $\equiv\text{Si}-\text{OH}$  are more reactive in respect to lithium ions than the bonds  $\equiv\text{C}-\text{X}$ ,  $\equiv\text{C}-\text{H}$ ,  $\equiv\text{C}-\text{OR}$  and  $\equiv\text{C}-\text{OH}$ . This  
15 leads to more rapid and complete coupling of the intermediate block copolymers. It should be noted that if dihydro - dialkyl - (aryl) - silanes are employed the final polymeric product will be free from traces of  
20 haloid.

The amount of coupling agent used depends on the physicochemical properties of

the required product. The necessary amount of coupling agent can be added at once or  
25 gradually.

The maximum effectiveness of the bifunctional compound is achieved if it is added in amounts from 0.5 to 5 or more equivalents to each equivalent of lithium ion, the optimum amount and the temperature and duration of the reaction being determined experimentally.  
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An advantage of the present invention is that depending on the nature of the substituent at the silicon atom it is possible to produce silicon-hydrocarbon polymers (polysilcarbanes) with a wide range of glass-transition temperatures from 50 to 180°C. The use of statistical (random) copolymers of vinyl derivatives of silicon and styrene or its derivatives for producing block A makes it possible to utilize such a cheap and readily available monomer as styrene, while being able to finely adjust the glass-transition temperature of block A over the temperature range from 95 to 180°C by adding a definite amount of styrene.  
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Below are given the glass-transition temperatures of some polymers based on vinyltriorganosilanes which are employed for producing block A.  
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	Polymer	Glass-transition temperature, °C
	Polyvinyltrimethylsilane	170-180
	Polyvinylphenyldimethylsilane	145-155
55	Polyvinylethyldimethylsilane	130-140
	Copolymer of vinylphenyldimethylsilane and styrene (molar ratio 1:1)	112-117
	Copolymer of vinylphenyldimethylsilane and styrene (molar ratio 1:3)	95-98

- 60 The process of the present invention can better be understood by reference to the following examples of several embodiments thereof.

#### EXAMPLE 1.

- 65 To 0.04 mol of vinyltrimethylsilane are added 33 ml. of cyclohexane and the mixture is heated to 35°C after which 0.0003 mol of secondary butyllithium is added. Polymerization is carried out in a reaction flask at a temperature of 35°C until the vinyltrimethylsilane has been completely exhausted.  
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The polyvinyltrimethylsilane has an intrinsic viscosity  $[\eta]=0.19$  dl/g (at 20°C in cyclohexane).

- 75 To the reaction mixture are added 0.10 mol of isoprene and 100 ml of cyclohexane, and polymerization carried out at 35°C until the isoprene has been completely exhausted.

- 80 The intermediate block copolymer produced has an intrinsic viscosity  $[\eta]=0.71$  dl/g (at 20°C in cyclohexane); the vinyltrimethylsilane content in the block-copolymer is 37.1% by weight.

To the intermediate block copolymer with living chains are now added 0.04 mol of vinyltrimethylsilane and 150 ml of cyclohexane and polymerization continued at 35°C until the vinyltrimethylsilane has been completely exhausted.  
85

The final block copolymer produced is dissolved in cyclohexane, reprecipitated in isopropyl alcohol, filtered and dried to constant weight.  
90

The block copolymer obtained has an intrinsic viscosity  $[\eta]=0.79$  dl/g (at 20°C in cyclohexane) and a vinyltrimethylsilane content of 49.1% by weight.  
95

#### EXAMPLE 2.

To 0.015 mol of vinylphenyldimethylsilane and 0.024 mol of styrene are added 33 ml of heptane and the mixture is heated to 40°C after which 0.0004 mol of n-butyllithium is added. Copolymerization is carried out at 40°C until the monomers have been completely exhausted.  
100

The copolymer obtained has an intrinsic viscosity  $[\eta]=0.29$  dl/g (at 20°C in cyclohexane).  
105

hexane) and contains 47% by weight of vinylphenyldimethylsilane.

To the reaction mixture are then added 0.22 mol of isoprene and 200 ml of heptane, and polymerization carried out at 35°C until the isoprene has been completely exhausted.

The intermediate block copolymer has an intrinsic viscosity  $[\eta]=0.81$  dl/g (at 20°C in cyclohexane) and contains 14.1% by weight of vinylphenyldimethylsilane.

To the living chains of the intermediate block copolymer thus obtained are added 0.015 mol of vinylphenyldimethylsilane and 0.024 mol of styrene in 250 ml of heptane. Polymerization is continued at 40°C until the monomers have been completely exhausted.

The block copolymer produced is dissolved in heptane and reprecipitated in ethyl alcohol, filtered and dried to constant weight.

The block copolymer has an intrinsic viscosity  $[\eta]=0.89$  dl/g (at 20°C in cyclohexane) and a vinylphenyldimethylsilane content of 20.9% by weight.

#### EXAMPLE 3

The process is carried out as in Example 2 but each block A is formed from a mixture of monomers: 0.015 mol of vinyltrimethylsilane and 0.048 mol of styrene.

The final block copolymer has an intrinsic viscosity  $[\eta]=0.80$  dl/g (at 20°C in cyclohexane) and a vinyltrimethylsilane content of 11.5% by weight.

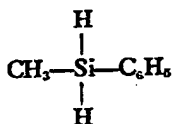
#### EXAMPLE 4.

To 0.04 mol of vinyltrimethylsilane are added 50 ml of cyclohexane and the mixture is heated to 30°C, after which 0.0004 mol of sec. amyllithium is added. Polymerization is carried out at 30°C until the vinyltrimethylsilane is completely exhausted. The polymer obtained has an intrinsic viscosity  $[\eta]=0.22$  dl/g (at 20°C in cyclohexane).

To the reaction mixture are then added 0.092 mol of butadiene and 100 ml of cyclohexane, and polymerization continued at 25°C until the butadiene is completely exhausted.

The intermediate block copolymer obtained has an intrinsic viscosity  $[\eta]=0.48$  dl/g and a vinyltrimethylsilane content of 50% by weight.

To the living chains of the intermediate block copolymer is added 0.0004 mol of methylphenylsilane



as coupling agent, along with 100 ml of cyclohexane. The addition reaction is carried out at 50°C over a period of 5 hours.

The final block copolymer produced is dis-

solved in cyclohexane, reprecipitated in isopropyl alcohol, filtered and dried to constant weight. The final block copolymer has an intrinsic viscosity  $[\eta]=0.76$  dl/g and a vinyltrimethylsilane content of 50% by weight.

#### EXAMPLE 5.

To 0.062 mol of vinylphenyldimethylsilane are added 50 ml of benzene and the mixture heated to 50°C after which 0.0003 mol of ethyllithium is added. Polymerization is carried out at 50°C until the monomer is completely exhausted. The polymer obtained has an intrinsic viscosity  $[\eta]=0.30$  dl/g.

To the reaction mixture are added 0.456 mol of isoprene and 400 ml of benzene, and polymerization continued at 35°C until the isoprene is completely exhausted. The intermediate block copolymer has a viscosity  $[\eta]=0.79$  dl/g and a vinylphenyldimethylsilane content of 28.1% by weight.

To the living chains of the block copolymer is added 0.062 mol of vinylphenyldimethylsilane and 250 ml of benzene and polymerization continued at 50°C until the monomer is completely exhausted.

The block copolymer obtained is dissolved in benzene, reprecipitated in ethyl alcohol, filtered and dried to constant weight.

The final block copolymer has an intrinsic viscosity  $[\eta]=0.91$  dl/g (at 20°C in cyclohexane) and a vinylphenyldimethylsilane content of 40.5% by weight.

#### EXAMPLE 6.

To 0.0085 mol of vinylbutyldimethylsilane are added 20 ml of benzene and the mixture heated to 45°C, after which 0.0004 mol of sec. butyllithium is added. Polymerization is carried out at 45°C until the monomer is completely exhausted.

The polymer obtained has a viscosity  $[\eta]=0.12$  dl/g (at 20°C in cyclohexane).

To the reaction mixture are then added 0.32 mol of isoprene and 200 ml of benzene and polymerization carried out at 35°C until the isoprene is completely exhausted.

The intermediate block copolymer has an intrinsic viscosity  $[\eta]=0.71$  dl/g (at 20°C in cyclohexane) and a vinylbutyldimethylsilane content of 5.2% by weight.

To the living chains of the intermediate block copolymer is added 0.0085 mol of vinyl butyldimethylsilane in 40 ml of benzene and polymerization carried out at 45°C until the monomer is completely exhausted.

The block copolymer produced is dissolved in benzene, reprecipitated in ethyl alcohol, filtered and dried to constant weight.

The final block copolymer has an intrinsic viscosity  $[\eta]=0.73$  dl/g (at 20°C in cyclohexane) and a vinylbutyldimethylsilane content of 10% by weight.

## EXAMPLE 7.

0.22 mol of isoprene is dissolved in a mixture of 100 ml of benzene and 100 of toluene and heated to 35°C, after which 5 0.00057 g-atom of metallic lithium is added to the mixture. Polymerization is carried out at 35°C until the isoprene is completely exhausted.

The polyisoprene obtained has an intrinsic viscosity  $[\eta]=0.71$  dl/g (at 20°C in cyclohexane).

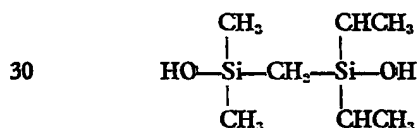
To the living polyisoprene chain, Li—B—Li, is added 0.04 mol of vinyl ethyldimethylsilane in a mixture of 50 ml of benzene and 50 ml of toluene and polymeriza- 15 tion continued at 50°C until the vinyl ethyldimethylsilane is completely exhausted.

The block copolymer obtained is dissolved in benzene, reprecipitated in methyl alcohol, filtered and dried to constant weight.

The final block copolymer has an intrinsic viscosity  $[\eta]=0.89$  dl/g (at 20°C in cyclohexane) and a vinyl ethyldimethylsilane content of 14.9% by weight.

## EXAMPLE 8.

The process is carried out as in Example 4, but the coupling agent employed is a bifunctional organosilicon-containing compound of the following structure:

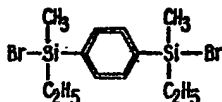


taken in fivefold excess in respect to lithium-ion, i.e., 0.002 mol.

The final block copolymer has an intrinsic viscosity  $[\eta]=0.78$  dl/g (at 20°C in cyclohexane) and a vinyltrimethylsilane content of 48% by weight.

## EXAMPLE 9.

The process is carried out as in example 4, but the monomer employed for producing 40 block A is vinylbutyldimethylsilane (0.04 mol) and the coupling agent is the following bifunctional silicon-containing compound:



45 taken in twofold excess in respect to lithium-ion, i.e., 0.0008 mol.

The final block copolymer has an intrinsic viscosity  $[\eta]=0.85$  dl/g (at 20°C in cyclohexane) and a vinylbutyldimethylsilane content of 49.5% by weight.

## EXAMPLE 10.

To 0.015 mol of vinylphenyldimethylsilane

and 0.015 mol of 2,4-dimethylstyrene are added 33 ml of cyclohexane and the mixture is heated to 40°C after which 0.0004 mol of n-butyllithium is added. Copolymerization is 55 carried out at 40°C until the monomers are completely exhausted.

The copolymer obtained has an intrinsic viscosity  $[\eta]=0.42$  dl/g and contains 54% by weight of vinylphenyldimethylsilane.

To the reaction mixture are then added 0.22 mol of isoprene and 200 ml of cyclohexane and polymerization carried out at 35°C until the isoprene is completely exhausted. The intermediate block copolymer 60 has an intrinsic viscosity  $[\eta]=0.86$  dl/g and a vinylphenyldimethylsilane content of 12.7% by weight.

To the living chains of the intermediate block copolymer obtained are added 0.015 mol of vinylphenyldimethylsilane and 0.015 mol of 2,4-dimethylstyrene, along with 250 ml of cyclohexane. Polymerization is carried out at 40°C until the complete exhaustion of the monomers.

The block copolymer obtained is dissolved in cyclohexane and reprecipitated in ethyl alcohol, filtered and dried to constant weight. The final block copolymer has an intrinsic viscosity  $[\eta]=0.91$  dl/g and a vinylphenyldimethylsilane content of 19.2% by weight.

## WHAT WE CLAIM IS:—

1. Elastomeric block copolymers of the A—B—A type, in which block B is a polymer of a conjugated diene, and block A is a polymer of a vinyltriorganosilane or a copolymer of a vinyltriorganosilane and styrene or a substituted styrene, said block A having an average molecular weight of from 5,000 to 200,000 and a glass-transition temperature of from 95 to 180°C.

2. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a polymer of vinylphenyldimethylsilane.

3. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a polymer of vinyl ethyldimethylsilane.

4. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a polymer of vinylbutyldimethylsilane.

5. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a polymer of vinyltrimethylsilane.

6. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a copolymer of vinyl phenyldimethylsilane and styrene.

7. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a copolymer of vinyltrimethylsilane and styrene.

8. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a copolymer of vinyl ethyldimethylsilane and styrene.

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9. An elastomeric block copolymer as claimed in Claim 1, wherein each block A is a copolymer of vinylbutyldimethylsilane and styrene.

5 10. Elastomeric block copolymers as claimed in any one of Claims 1 to 9 wherein the blocks A constitute from 10 to 50% by weight of the block copolymer.

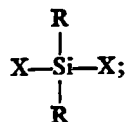
11. Elastomeric block copolymers according to Claim 1 and substantially as hereinbefore described.

12. A method of producing a block copolymer of the A—B—A type as claimed in any one of Claims 1 to 11, comprising  
15 block copolymerizing a conjugated diene with a vinyltriorganosilane or a mixture of a vinyltriorganosilane and styrene or a substituted styrene in the presence of a lithium or organolithium catalyst.

20 13. A method as claimed in Claim 12, including the steps of polymerizing a vinyltriorganosilane or copolymerizing a vinyltriorganosilane and styrene or a substituted styrene to form polymer block A having a molecular weight of from 5,000 to 200,000  
25 adding a conjugated diene and continuing the polymerization to form block B having a molecular weight of 15,000 to 500,000, after which a further addition is made of said  
30 vinyltriorganosilane or a mixture of vinyltriorganosilane and styrene or a substituted styrene.

35 14. A method as claimed in Claim 12, including the steps of polymerizing a vinyltriorganosilane or copolymerizing a vinyltriorganosilane and styrene or a substituted styrene to form polymer block A having a molecular weight of from 5,000 to 200,000,  
40 adding a conjugated diene and continuing the polymerization to form block B having a molecular weight of 7,500 to 250,000 and then adding a bifunctional organosilicon compound.

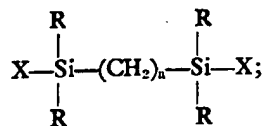
45 15. A method as claimed in Claim 14, wherein the bifunctional organosilicon compound has the structure



50 where X is Br, Cl, OR, OH or H, and the groups R, the same or different, represent normal or branched alkyl radicals with 1 to 16

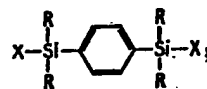
carbon atoms, aryl radicals, substituted aryl radicals or naphthenic radicals.

16. A method as claimed in Claim 14, wherein the bifunctional organosilicon compound has the structure



where  $n=1-6$ , X is Br, Cl, OR, OH or H and the groups R the same or different, represent normal or branched alkyl radicals with 1 to 16 carbon atoms, aryl radicals, substituted aryl radicals or naphthenic radicals.

17. A method as claimed in Claim 14, wherein the bifunctional organosilicon compound has the structure



where X is Br, Cl, OR, OH or H and the groups R the same or different, represent normal or branched alkyl radicals with 1 to 16 carbon atoms, aryl radicals, substituted aryl radicals or naphthenic radicals.

18. A method as claimed in Claim 12, wherein the conjugated diene is first polymerized in the presence of metallic lithium to form an intermediate block Li—B—Li having lithium atoms at the ends of the polymer chains, after which a vinyltriorganosilane or a mixture of vinyltriorganosilane and styrene or a substituted styrene is added and polymerization continued to form the final block copolymer A—B—A.

19. A method of producing block copolymers of the A—B—A type as claimed in Claim 1, according to any one of the Examples.

20. Elastomeric block copolymers whenever produced by the method of any one of Claims 12 to 19.

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